

Appendix A

Support in the Specification of U.S. Patent No. 6,110,881¹ for the Claims Presented Herein

Applicants' Claims	Applicants' Disclosure
<p>64. (New) A method for removing etching and resist material from a multi-level substrate, comprising the steps of:</p> <ul style="list-style-type: none"> (a) forming a photoresist layer on a substrate level comprising a metal; (b) exposing a portion of the photoresist layer, leaving a portion of the photoresist layer unexposed, and removing unreacted photoresist so that a resist pattern is formed; (c) etching at least a portion of the substrate, using the resist pattern as a mask; and 	<p>(page 2, line 23 through page 3, line 4)</p> <p>Positive-type resists have been extensively used as masking materials to delineate patterns onto a substrate so that the patterns can be subsequently etched or otherwise defined into the substrate. The final steps in preparing the substrate then involve removing the unexposed resist material and any etching residue from the substrate. (page 3, lines 18-22)</p> <p>Additionally, during such etching processing, an organometallic by-product compound can be formed on the sidewall of the substrate material. The above-mentioned solvents are also ineffective in removing such organometallic polymers. (page 5, lines 10-13)</p> <p>More specifically, during the fabrication of microcircuits, the substrate surface can be aluminum, titanium, silicon oxide or polysilicon and patterns are delineated thereon by chemical etching.</p>
<p>(d) contacting the etched substrate with a cleaning composition at a temperature of between about room temperature and 100°C, to remove the resist pattern and etching residue from the etched substrate,</p>	<p>(page 25, line 17 through page 26, line 2)</p> <p>The method of removing a resist from a substrate or cleaning etching residue from a substrate using the compositions of the present invention involves contacting a substrate having a material to be removed with a composition of the present invention for a time and at a temperature sufficient to remove the residue. The substrate is immersed in the composition. The time and temperature of immersion are determined based on the particular material being removed from a substrate. Generally, the temperature is in the range of from about room temperature to 100°C and the contact time is from about 2 to 60 minutes.</p>

¹ The instant application claims priority as a continuation of U.S. Application Serial No. 09/988,545, filed November 20, 2001, which is a continuation of U.S. Application Serial No. 09/603,693, filed June 26, 2000, now U.S. Patent No. 6,319,885, which is a continuation of U.S. Application Serial No. 08/654,007, filed May 28, 1996, now U.S. Patent No. 6,110,881 which is a continuation of application SN 08/078,657, filed June 21, 1993, now abandoned.

<p>wherein the cleaning composition comprises:</p> <p>(a) from about 5% to 50% by weight of hydroxylamine or a derivative thereof having a general formula of:</p> $(R_1R_2)N-OR_3$ <p>wherein R_1, R_2, and R_3 are independently hydrogen; a hydroxyl group; a C_1-C_6 straight, branched or cyclo alkyl, alkenyl, or alkynyl group; an acyl group; a straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group; or a salt thereof;</p>	<p>(Page 18, lines 3-11)</p> <p>The cleaning composition preferably includes from about 5% to 50% by weight of at least one nucleophilic amine compound having reduction and oxidation potentials, from about 10% to about 80% by weight of at least one organic solvent which is miscible with the nucleophilic amine compound, optionally from about 5%-30% by weight of at least one chelating agent, and with the remaining balance of the composition being made up of water, preferably high purity deionized water. (page 19, lines 12-22)</p> <p>Specific examples of nucleophilic amine compounds are further described below. Hydroxylamines suitable for use as the nucleophilic amine compound having reduction and oxidation potentials are represented by the following formula:</p> $(R_1R_2)N-OR_3$ <p>wherein R_1, R_2, and R_3 are independently hydrogen; a hydroxyl group; optionally a substituted C_1-C_6 straight, branched or cyclo alkyl, alkenyl, or alkynyl group; optionally a substituted acyl group, straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group, or the salt of such compounds.</p>
<p>(b) from about 10% to 80% by weight of at least one organic solvent miscible with the hydroxylamine or the hydroxylamine derivative;</p>	<p>(Page 18, lines 3-11)</p> <p>The cleaning composition preferably includes from about 5% to 50% by weight of at least one nucleophilic amine compound having reduction and oxidation potentials, from about 10% to about 80% by weight of at least one organic solvent which is miscible with the nucleophilic amine compound, optionally from about 5%-30% by weight of at least one chelating agent, and with the remaining balance of the composition being made up of water, preferably high purity deionized water.</p>

<p>(c) from about 5% to 30% by weight of an aromatic hydroxy-functional compound having a general formula of:</p> $(HO)_n-Ph-R_m$ <p>wherein n=1-4, m=2-5 and each R is independently hydrogen; a C₁-C₆ straight, branched or cyclo alkyl, alkenyl, or alkynyl group; an acyl group; a straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group; or a salt thereof; and</p>	<p>(Page 18, lines 3-11)</p> <p>The cleaning composition preferably includes from about 5% to 50% by weight of at least one nucleophilic amine compound having reduction and oxidation potentials, from about 10% to about 80% by weight of at least one organic solvent which is miscible with the nucleophilic amine compound, optionally from about 5%-30% by weight of at least one chelating agent, and with the remaining balance of the composition being made up of water, preferably high purity deionized water. (page 16, lines 13-18)</p> <p>In a composition according to the invention, the composition preferably contains a chelating agent. The chelating serves to provide long term stability and activity to the composition. The composition, therefore, has the desirable commercial attribute of having a long shelf life. (page 23, lines 4-16)</p> <p>Preferred chelating agents useful in the composition of the invention are hydroxybenzenes according to the formula –</p> $(HO)_n-Ph-R_m$ <p>wherein n=1-4, m=2-5 and R is independently hydrogen; optionally a substituted C₁-C₆ straight, branched or cyclo alkyl, alkenyl, or alkynyl group; optionally a substituted acyl group, straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group; or the salt of such compounds. The preferred compounds are the dihydroxybenzene isomers, and the alkyl substituted dihydroxybenzenes. The most preferred compounds are 1,2-dihydroxybenzene and 1,2-dihydroxy-4-t-butylbenzene. (page 16, lines 2-12)</p>
<p>(d) water.</p>	<p>The cleaning and stripping composition of the present invention for removing etching residue and resists from a substrate contains at least one nucleophilic amine compound having oxidation and reduction potentials in a cleaning environment, at least one organic solvent which is miscible with the nucleophilic amine compound, water, and, optionally, one or more chelating agents. The water can be provided in the composition independently or in combination with the nucleophilic amine compounds, for example the nucleophilic amine compound can be added as a 50% aqueous solution.</p>

<p>65. (New) The method of claim 64, wherein the hydroxylamine or derivative thereof comprises hydroxylamine, which is added as a 50% aqueous solution.</p>	<p>(page 16, lines 8-12) The water can be provided in the composition independently or in combination with the nucleophilic amine compounds, for example the nucleophilic amine compound can be added as a 50% aqueous solution. (page 16, line 25 through page 17, line 1) As stated above, the water can be present in combination with the nucleophilic amine compound. (page 24, line 21 through page 25, line 1) A presently most preferred cleaning composition of the invention comprises, based on the total weight of the composition, 35 parts hydroxylamine, 65 parts 2-amino-2-ethoxyethanol, and 5 parts 1,2-dihydroxybenzene, wherein the hydroxylamine is present as a 50% aqueous solution.</p>
<p>66. (New) The method of claim 64, wherein the composition comprises more than one organic solvent.</p>	<p>(page 21, lines 22-23) Preferably an amine solvent is present alone or in combination with another solvent. Previously, it had been believed that an alkanolamine solvent had to be utilized.</p>
<p>67. (New) The method of claim 66, wherein: (a) the hydroxylamine or derivative thereof comprises hydroxylamine or an alkyl or carboxyl substituted hydroxylamine derivative;</p>	<p>(page 19, lines 12-22) Specific examples of nucleophilic amine compounds are further described below. Hydroxylamines suitable for use as the nucleophilic amine compound having reduction and oxidation potentials are represented by the following formula: $(R_1R_2)N-OR_3$ wherein R_1, R_2, and R_3 are independently hydrogen; a hydroxyl group; optionally a substituted C_1-C_6 straight, branched or cyclo alkyl, alkenyl, or alkynyl group; optionally a substituted acyl group, straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group, or the salt of such compounds. (page 21, lines 5-8) The preferred nucleophilic amine compounds having reduction and oxidation potentials are alkoxy substituted amines, hydroxylamine, alkyl or carboxyl substituted hydroxylamine, and alkyl or carboxyl substituted hydrazine.</p>

<p>(b) the more than one organic solvent comprises:</p> <p>(1) an alkanolamine selected from the group consisting of monoethanolamine, diethanolamine, triethanolamine, tert-butyl diethanolamine, isopropanolamine, 2-amino-1-propanol, 3-amino-1-propanol, isobutanolamine, 2-amino-2-ethoxy-propanol, and diglycolamine; and</p>	<p>(page 21, lines 22-23) Preferably an amine solvent is present alone or in combination with another solvent. Previously, it had been believed that an alkanolamine solvent had to be utilized. (page 22, lines 12-17) Examples of suitable alkanolamines include monoethanolamine, diethanolamine, triethanolamine, tert-butyl diethanolamine, isopropanolamine, 2-amino-1-propanol, 3-amino-1-propanol, isobutanolamine, 2-amino-2-ethoxy-propanol, and 2-amino-2-ethoxy-ethanol, which is also known as diglycolamine.</p>
<p>(2) a non-amine solvent selected from the group consisting of dimethylsulfoxide, N-methyl-2-pyrrolidinone, N,N-dimethylpropanamide, N,N-dimethylformamide, ethylene glycol, ethylene glycol alkyl ether, diethylene glycol alkyl ether, triethylene glycol alkyl ether, propylene glycol, propylene glycol alkyl ether, dipropylene glycol alkyl ether, tripropylene glycol alkyl ether, and N-substituted pyrrolidone; and</p>	<p>(page 22, line 18 through page 23, line 1) Additional examples of organic solvents suitable for use in the composition of the present invention include N-methyl-2-pyrrolidinone, N,N-dimethylpropanamide, N,N-dimethylformamide, ethylene glycol, ethylene glycol alkyl ether, diethylene glycol alkyl ether, triethylene glycol alkyl ether, propylene glycol, propylene glycol alkyl ether, dipropylene glycol alkyl ether, tripropylene glycol alkyl ether, N-substituted pyrrolidone, ethylenediamine, and ethylenetriamine. (page 21, lines 20-21) Additionally, non-amine solvents, such as dimethylsulfoxide (DMSO), are suitable for use.</p>
<p>(c) the aromatic hydroxy-functional compound comprises a dihydroxybenzene.</p>	<p>(page 23, lines 4-16) Preferred chelating agents useful in the composition of the invention are hydroxybenzenes according to the formula – $(HO)_n-Ph-R_m$ wherein n=1-4, m=2-5 and R is independently hydrogen; optionally a substituted C₁-C₆ straight, branched or cyclo alkyl, alkenyl, or alkynyl group; optionally a substituted acyl group, straight or branched alkoxy group, amide group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group; or the salt of such compounds. The preferred compounds are the dihydroxybenzene isomers, and the alkyl substituted dihydroxybenzenes. The most preferred compounds are 1,2-dihydroxybenzene and 1,2-dihydroxy-4-t-butylbenzene. (page 22, lines 4-6) Suitable alkanolamines are primary, secondary or tertiary amines and are preferably monoamines, diamines or triamines, and, most preferably, monoamines.</p>
<p>68. (New) The method of claim 67, wherein the at least one organic solvent comprises (1) a monoamine and (2) dimethylsulfoxide.</p>	

	(page 21, lines 20-21) Additionally, non-amine solvents, such as dimethylsulfoxide (DMSO), are suitable for use.
69. (New) The method of claim 68, wherein the monoamine is at least one selected from the group consisting of monoethanolamine and diglycolamine.	(page 21, lines 19-20) Suitable organic solvents include alkanolamines and their derivatives. (see Table I, page 27, Compositions A-G for specific Examples using monoethanolamine and diglycolamine)
70. (New) The method of claim 69, wherein the monoamine consists essentially of monoethanolamine.	(see Table I, page 27, Compositions D and F for specific Examples using monoethanolamine)
71. (New) The method of claim 67, wherein the hydroxylamine or derivative thereof comprises hydroxylamine.	(page 21, lines 5-11) The preferred nucleophilic amine compounds having reduction and oxidation potentials are alkoxy substituted amines, hydroxylamine, alkyl or carboxyl substituted hydroxylamine, and alkyl or carboxyl substituted hydrazine. The most preferred compounds are hydroxylamine, N-methyl-hydroxylamine hydrochloride, N,N-diethylhydroxylamine, and methylhydrazine.
72. (New) The method of claim 70, wherein the hydroxylamine or derivative thereof comprises hydroxylamine.	(page 24, line 21 through page 25, line 1) A presently most preferred cleaning composition of the invention comprises, based on the total weight of the composition, 35 parts hydroxylamine, 65 parts 2-amino-2-ethoxyethanol, and 5 parts 1,2-dihydroxybenzene, wherein the hydroxylamine is present as a 50% aqueous solution.

<p>73. (New) The method of claim 67, wherein the aromatic hydroxy-functional compound comprises at least one of 1,2-dihydroxy-4-t-butylbenzene and 1,2-dihydroxybenzene.</p> <p>74. (New) The method of claim 70, wherein the aromatic hydroxy-functional compound comprises at least one of 1,2-dihydroxy-4-t-butylbenzene and 1,2-dihydroxybenzene.</p> <p>75. (New) The method of claim 72, wherein the aromatic hydroxy-functional compound comprises at least one of 1,2-dihydroxy-4-t-butylbenzene and 1,2-dihydroxybenzene.</p>	<p>(page 23, lines 4-16) Preferred chelating agents useful in the composition of the invention are hydroxybenzenes according to the formula – $(HO)_n-Ph-R_m$ wherein $n=1-4$, $m=2-5$ and R is independently hydrogen; optionally a substituted C_1-C_6 straight, branched or cyclo alkyl, alkenyl, or alkynyl group; optionally a substituted acyl group, straight or branched alkoxy group, amidyl group, carboxyl group, alkoxyalkyl group, alkylamino group, alkylsulfonyl group, or sulfonic acid group; or the salt of such compounds. The preferred compounds are the dihydroxybenzene isomers, and the alkyl substituted dihydroxybenzenes. The most preferred compounds are 1,2-dihydroxybenzene and 1,2-dihydroxy-4-t-butylbenzene. (page 24, line 21 through page 25, line 1) A presently most preferred cleaning composition of the invention comprises, based on the total weight of the composition, 35 parts hydroxylamine, 65 parts 2-amino-2-ethoxyethanol, and 5 parts 1,2-dihydroxybenzene, wherein the hydroxylamine is present as a 50% aqueous solution.</p> <p>(see Table I, page 27, Compositions C-F)</p>
<p>76. (New) The method of claim 64, wherein the cleaning composition comprises from 30% to 60% by weight of the at least one organic solvent miscible with the hydroxylamine or hydroxylamine derivative.</p>	
<p>77. (New) The method of claim 64, wherein the contacting of the etched substrate with the cleaning composition is performed for about 2 to 60 minutes.</p>	<p>(page 26, lines 1-2) Generally, the temperature is in the range of from about room temperature to 100°C and the contact time is from about 2 to 60 minutes.</p>
<p>78. (New) The method of claim 77, wherein the contacting of the etched substrate with the cleaning composition is a two step process, the first step comprising contacting for about 30 minutes at a temperature of about 65°C, and the second step comprising contacting for about 10 minutes at a temperature from about 80-85°C.</p>	<p>(page 26, lines 2-8) A preferred method involves immersing a substrate sample, such as a wafer in the solution of the invention for 30 minutes at a temperature of about 65°C followed by placement of the substrate sample in a solvent bath for 10 minutes at about 80°-85°C and, thereafter, rinsing the substrate sample in a water bath.</p>

<p>79. (New) A method for removing etching and resist material from a multi-level substrate, comprising the steps of:</p> <p>(a) forming a photoresist layer on a substrate level comprising a metal;</p> <p>(b) exposing a portion of the photoresist layer, leaving a portion of the photoresist layer unexposed, and removing unreacted photoresist so that a resist pattern is formed;</p> <p>(c) etching at least a portion of the substrate, using the resist pattern as a mask; and</p>	<p>(page 2, line 23 through page 3, line 4)</p> <p>Positive-type resists have been extensively used as masking materials to delineate patterns onto a substrate so that the patterns can be subsequently etched or otherwise defined into the substrate. The final steps in preparing the substrate then involve removing the unexposed resist material and any etching residue from the substrate. (page 3, lines 18-22)</p> <p>Additionally, during such etching processing, an organometallic by-product compound can be formed on the sidewall of the substrate material. The above-mentioned solvents are also ineffective in removing such organometallic polymers. (page 5, lines 10-13)</p> <p>More specifically, during the fabrication of microcircuits, the substrate surface can be aluminum, titanium, silicon oxide or polysilicon and patterns are delineated thereon by chemical etching.</p>
<p>(d) contacting the etched substrate with a cleaning composition at a temperature of between about room temperature and 100°C, to remove the resist pattern and etching residue from the etched substrate,</p>	<p>(page 25, line 17 through page 26, line 2)</p> <p>The method of removing a resist from a substrate or cleaning etching residue from a substrate using the compositions of the present invention involves contacting a substrate having a material to be removed with a composition of the present invention for a time and at a temperature sufficient to remove the residue. The substrate is immersed in the composition. The time and temperature of immersion are determined based on the particular material being removed from a substrate. Generally, the temperature is in the range of from about room temperature to 100°C and the contact time is from about 2 to 60 minutes.</p>

<p>wherein the cleaning composition consists essentially of:</p> <p>(1) about 17.5 parts of hydroxylamine;</p> <p>(2) about 27 parts of an alkanolamine solvent;</p> <p>(3) about 5 parts of 1,2-dihydroxybenzene;</p> <p>(4) about 33 parts of dimethylsulfoxide solvent; and</p> <p>(5) from about 17.5 to about 37.5 parts water.</p>	<p>(page 38, lines 7-20)</p> <p><u>Example 16</u></p> <p>A cleaning solution including 35 parts hydroxylamine (50% aqueous), 27 parts DGA, 5 parts catechol, and 33 parts DMSO was prepared and utilized to clean a wafer. The wafer had a polysilicon structure and was completely cleaned with no damage to the structure by the cleaning solution. Wafers containing via holes also were cleaned of plasma etching residue.</p> <p>The cleaning solution was thereafter diluted with 20 parts water and fresh wafer samples cleaned utilizing the solution. The addition of water did not reduce the ability of the solution to clean polysilicon structures. The etching residue was satisfactorily removed from the wafer samples.</p>
<p>80. (New) The method of claim 79, wherein the contacting of the etched substrate with the cleaning composition is performed for about 2 to 60 minutes.</p>	<p>(page 26, lines 1-2)</p> <p>Generally, the temperature is in the range of from about room temperature to 100°C and the contact time is from about 2 to 60 minutes.</p>
<p>81. (New) The method of claim 80, wherein the contacting of the etched substrate with the cleaning composition is a two step process, the first step comprising contacting for about 30 minutes at a temperature of about 65°C, and the second step comprising contacting for about 10 minutes at a temperature from about 80-85°C.</p>	<p>(page 26, lines 2-8)</p> <p>A preferred method involves immersing a substrate sample, such as a wafer in the solution of the invention for 30 minutes at a temperature of about 65°C followed by placement of the substrate sample in a solvent bath for 10 minutes at about 80°-85°C and, thereafter, rinsing the substrate sample in a water bath.</p>
<p>82. (New) The method of claim 79, wherein the alkanolamine is a monoamine.</p>	<p>(page 22, lines 4-6)</p> <p>Suitable alkanolamines are primary, secondary or tertiary amines and are preferably monoamines, diamines or triamines, and, most preferably, monoamines.</p>
<p>83. (New) The method of claim 82, wherein the monoamine is at least one selected from the group consisting of monoethanolamine and diglycolamine.</p>	<p>(page 21, lines 19-20)</p> <p>Suitable organic solvents include alkanolamines and their derivatives. (see Table I, page 27, Compositions A-G for specific Examples using monoethanolamine and diglycolamine)</p>
<p>84. (New) The method of claim 83, wherein the monoamine consists essentially of monoethanolamine.</p>	<p>(see Table I, page 27, Compositions D and F for specific Examples using monoethanolamine)</p>

85. (New) The method of claim 79, wherein the substrate layer comprises titanium.	(page 5, lines 3-9) The requirement for a cleaning solution to remove all types of residue generated as a result of plasma etching of various types of metals, such as aluminum, aluminum/silicon/ copper, titanium, titanium nitride, titanium/tungsten, tungsten, silicon oxide, polysilicon crystal, etc., presents a need for more effective cleaning chemistry in the processing area.
86. (New) The method of claim 79, wherein the substrate layer comprises aluminum.	
87. (New) The method of claim 79, wherein the substrate layer comprises tungsten.	
88. (New) The method of claim 79, further comprising ashing the resist and etching residue after the step of etching.	(page 3, lines 5-19) Increasingly, however, plasma etching, reactive ion etching or ion milling is used to define the pattern in a substrate which renders the resist mask substantially impossible to remove by stripping agents heretofore commonly used for such or similar purposes (page 3, line 22 through page 4, line 2) A recently developed technique effective for photoresist removal is plasma oxidation, also known as plasma ashing. However, while this process is effective for removing a photoresist, it is not effective for removing the organometallic polymer formed on the sidewall of the substrate during the etching process. (page 28, lines 1-10) <u>Example 1</u> Example 1 illustrates the problem of residue remaining on a wafer substrate following plasma etching and ashing. FIGURE 1 shows etched wafer residue present on an etched substrate following plasma ashing. Specifically, silicon oxide used as a dielectric layer has a pattern etched for a multi-layer interconnect according to a standard plasma etching process. A photoresist which was used as a masking material has already been removed by oxygen plasma ashing.
89. (New) The method of claim 88, wherein the substrate layer comprises titanium.	(page 5, lines 3-9) The requirement for a cleaning solution to remove all types of residue generated as a result of plasma etching of various types of metals, such as aluminum, aluminum/silicon/ copper, titanium, titanium nitride, titanium/tungsten, tungsten, silicon oxide, polysilicon crystal, etc., presents a need for more effective cleaning chemistry in the processing area.
90. (New) The method of claim 88, wherein the substrate layer comprises aluminum.	
91. (New) The method of claim 88, wherein the substrate layer comprises tungsten.	